Soft X-ray radiation damage in EM-CCDs used for Resonant Inelastic X-ray Scattering

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ABSTRACT: Advancement in synchrotron and free electron laser facilities means that X-ray beams with higher intensity than ever before are being created. The high brilliance of the X-ray beam, as well as the ability to use a range of X-ray energies, means that they can be used in a wide range of applications. One such application is Resonant Inelastic X-ray Scattering (RIXS).

RIXS uses the intense and tuneable X-ray beams in order to investigate the electronic structure of materials. The photons are focused onto a sample material and the scattered X-ray beam is diffracted off a high resolution grating to disperse the X-ray energies onto a position sensitive detector. Whilst several factors affect the total system energy resolution, the performance of RIXS experiments can be limited by the spatial resolution of the detector used. Electron-Multiplying CCDs (EM-CCDs) at high gain in combination with centroiding of the photon charge cloud across several detector pixels can lead to sub-pixel spatial resolution of 2-3 μm.

X-ray radiation can cause damage to CCDs through ionisation damage resulting in increases in dark current and/or a shift in flat band voltage. Understanding the effect of radiation damage on EM-CCDs is important in order to predict lifetime as well as the change in performance over time. Two CCD-97s were taken to PTB at BESSY II and irradiated with large doses of soft X-rays in order to probe the front and back surfaces of the device. The dark current was shown to decay over time with two different exponential components to it.

This paper will discuss the use of EM-CCDs for readout of RIXS spectrometers, and limitations on spatial resolution, together with any limitations on instrument use which may arise from X-ray-induced radiation damage.

KEYWORDS: EM-CCD; RIXS; X-ray; Radiation damage.

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Contents

1. Resonant Inelastic X-ray Scattering

Resonant Inelastic X-ray Scattering (RIXS) is a spectroscopic technique by which the electronic structure of materials can be studied. RIXS is often described as a "photon-in photon-out" process [1]. That is, an incident photon interacts with an atom in the target sample, exciting an electron into a higher energy level. An electron from a different energy level then relaxes into the unoccupied state, emitting an X-ray photon in the process. The emitted X-ray will therefore have different properties to that of the incident photon.

RIXS has a number of advantages over other spectroscopic techniques. These include the bulk sensitivity of RIXS; the X-rays have sufficient absorption length which means they are able to penetrate the surface layers of the sample and probe excitations in the bulk. Also, the incident photon energy can be chosen such that it resonates with certain atomic transitions within the sample (absorption edges) so that specific sample atomic sites can be probed. Thirdly, although the relative cross section of RIXS is small, higher brilliance X-ray sources with efficient focussing optics are built [2], and X-rays in general have a higher interaction cross-section than neutrons [3], therefore the sample being studied can have a very small volume.

A common RIXS spectrometer design [4] is to use a grating with variable line spacing to disperse the X-rays across a Charge-Coupled Device (CCD). There are a number of limitations to the overall performance of this spectrometer design. The two main contributions to the resolution are from the grating manufacturing inaccuracy, and the spatial resolution of the detector used. Figure 1 shows the energy resolution of the RIXS spectrometer at the Swiss Light Source (SLS) synchrotron at the Paul Scherrer Institute (PSI) before an upgrade process began in 2010. The spectrometer used a grating with 3200 lines/mm (slope error = 0.67 μrad rms) and a CCD detector (spatial resolution = 25 μm) [5][6]. A few ways that the resolution of RIXS spectrometers can be improved is to increase the accuracy of the grating, as well as increasing the spatial resolution of the CCD.

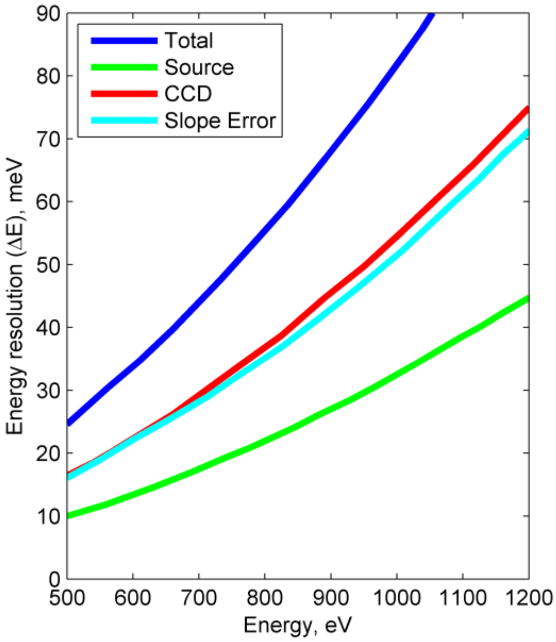

Figure 1. Energy resolution of the RIXS spectrometer at PSI before an upgrade process began in 2010, from [5].

2. The CCD and centroiding of X-ray events

A detailed description of the structure and operation of a Charge-Coupled Device (CCD) can be found in the literature [7][8], however a brief overview of the X-ray imaging process will be described here. When a photon interacts with the silicon of the CCD, a number of electron-hole pairs will be generated via the photoelectric effect. If this photon interacts in the field free region of the CCD, the charge diffuses outwards, until entering the depleted region and drifting towards the closest pixel's potential well [9].

As the electrons diffuse in the field free region, the charge cloud from a single X-ray photon will spread out. The size of this charge cloud when it is collected in the electrode potential depends on how far into the field free region it originated from. Figure 2(a) shows that when an X-ray penetrates deep into the device it will create a charge cloud close to the pixel electrodes. Therefore, the charge cloud is likely to be contained within a single pixel. Figure 2(b) shows that when an X-ray interacts far away from the electrode structure the charge cloud will have time to diffuse outwards so that the charge is spread across multiple pixels. Due to the diffusion of the electron charge cloud in the field free region, the spatial resolution of the CCD has been determined to be independent of pixel size and has been experimentally found to be have a limit of 25 μm for common back-thinned CCDs [10]. However, an analysis technique has been developed to achieve a resolution better than 25 μm by centroiding the X-ray events.

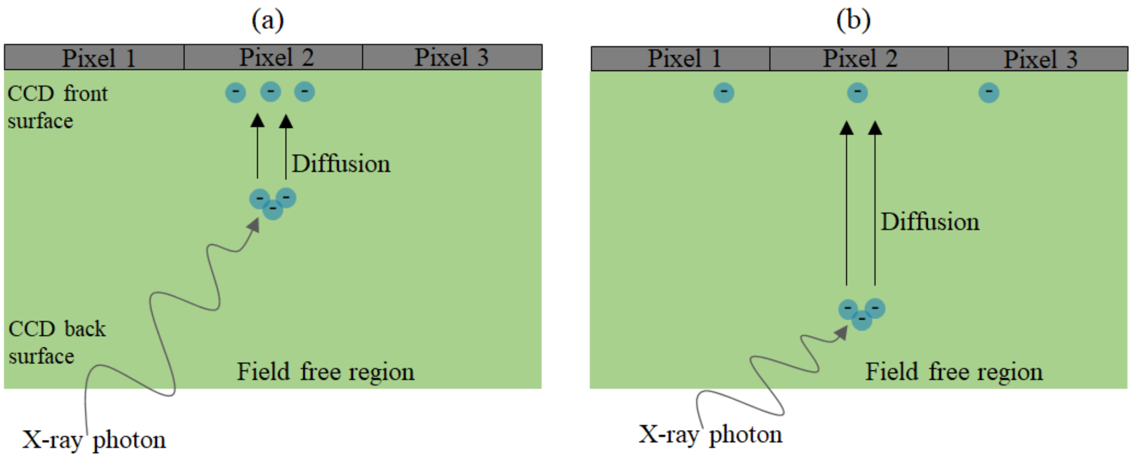

Figure 2. (a) The X-ray interacts in the field free region of silicon close to the front surface of the CCD and the charge cloud is contained within one pixel. (b) The X-ray interacts close to the back surface of the CCD and the charge cloud spreads across multiple pixels.

The charge cloud distribution is approximately symmetrical and centred on the point of maximum charge density. As a result, a "centre of mass" correction can be applied. Experimental results have shown that the intrinsic limit on the spatial resolution of a conventional CCD can be increased from 25 μm to a worst-case resolution of better than 4.7 μm (FWHM) if operated in photon counting mode with the "centre of mass" centroiding applied [11]. Photon counting mode relies upon a very low readout noise so that the charge cloud created by a single photon can be differentiated from the noise of the CCD. While photon counting with a conventional CCD can be done, the throughput of the spectrometer will be reduced by a factor of approximately 2.2 [12] as the CCD will have to be read out at a slower rate (100 kPixel/s for the camera that was used at PSI) in order to have an low enough noise of 3.84 e-rms. The CCD can be read out faster, however this results in an increased readout noise of 10.8 e-rms, eliminating the possibility of detecting single photon events. Therefore, centroiding with a conventional CCD was not a viable option for improving the performance of RIXS spectrometers while maintaining a high throughput.

3. EM-CCDs and their effect on resolution of RIXS spectrometers

An Electron-Multiplying CCD (EM-CCD) has the same basic structure as that of a conventional CCD, with additional elements added to the readout register as shown in Figure 3. The additional register elements, known as multiplication elements, have a different operational clocking scheme than a normal pixel. Figure 4 shows the potential well diagram of a multiplication element in the readout register of an EM-CCD. One of the four electrodes, Rφ2HV, is operated at a high voltage (usually between 30 V and 40 V [13]) which has the effect of accelerating the electrons, giving them enough energy to free bound electrons in the silicon lattice, increasing the signal in that element. These newly liberated electrons may then free more electrons, leading to an avalanche effect, increasing the signal by factors up to 10000 [14]. The multiplication elements are located before the readout node, i.e. before any noise is added by electron to voltage conversion process, essentially reducing the read noise of the EM-CCD.

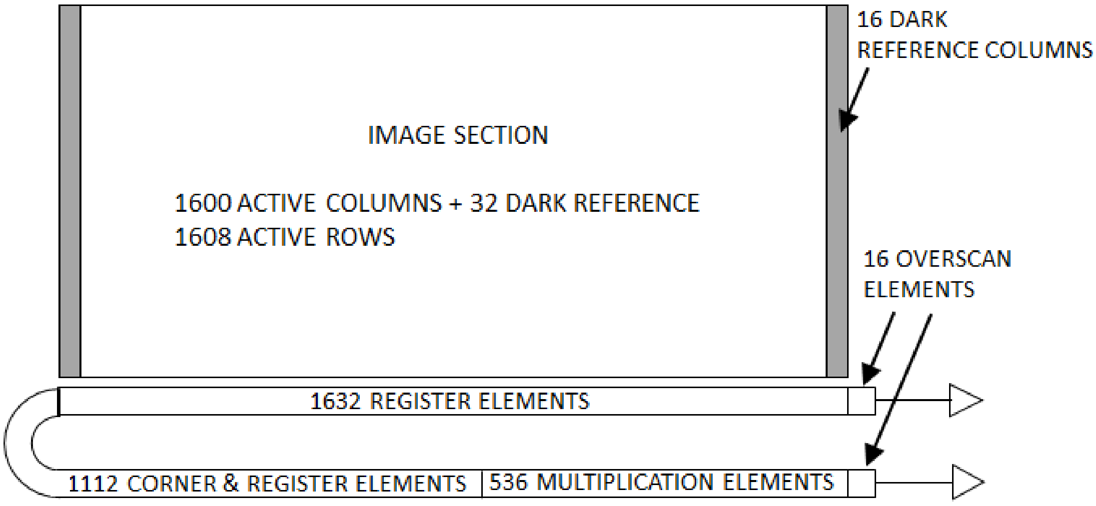

Figure 3. Schematic diagram of the CCD207-40 showing the 536 multiplication elements involved in the avalanche gain process, adapted from [15].

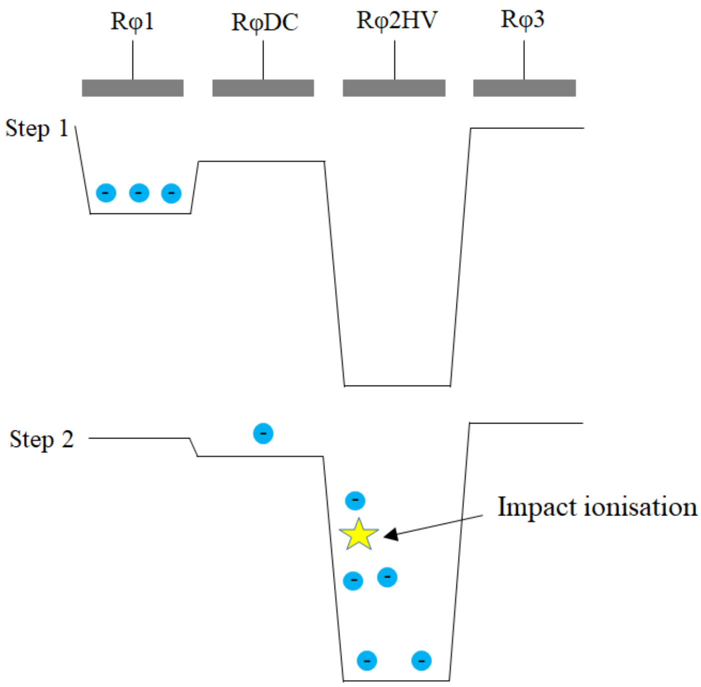

Figure 4. Potential well diagram of a multiplication gain element in an EM-CCD readout register.

Due to the additional multiplication elements of the readout register of an EM-CCD, the readout noise is reduced to < 1 electron rms. The low noise performance means that EM-CCDs can be operated in photon counting mode, at MHz pixel rates. As a result, the increased resolution obtained by centroiding single X-ray events can be achieved using an EM-CCD with short integrations and fast readout times. Initial results showed that at 380 eV the resolution achievable with an EM-CCD was better than 3 μm [16]. Further work at higher energies of 850 eV and 1000 eV showed the resolution can be better than 2.2 μm [17]. The additional multiplication elements add an extra source of noise due to the stochastic nature of the multiplication process. The effect of this noise source on X-ray detection in EM-CCDs is discussed in the literature [18][19].

4. Soft X-ray radiation damage in EM-CCDs

As discussed above, an EM-CCD can provide a much improved spatial resolution performance for use with a RIXS spectrometer without reducing throughput. As the newest generation of cameras at RIXS beamlines are using EM-CCDs, it is important to understand how their performance will change over time. A potential concern is the radiation damage effect of soft X-rays on EM-CCDs.

X-rays are generally too low in energy to cause bulk damage to CCDs and the damage mechanism of X-rays in CCDs is through ionising dose. Ionising radiation can induce flat band voltage shifts through ionising the dielectric or produce dark current generation centres by creating traps at the silicon-dielectric interface. The interface between the silicon lattice and the silicon dioxide insulating layer will have mismatches in atoms leading to dangling bonds (as shown in Figure 5). Any dangling bonds are usually rendered inactive due to a hydrogen anneal in the manufacturing of the CCD. An X-ray can interact with the silicon and SiO_2 to create an electron-hole pair. Holes can recombine with a bonding electron at the interface, liberating a hydrogen bonded at the mismatch in atoms at the Si-SiO_2 interface. Multiple hydrogen atoms can combine into molecular hydrogen (H_2) which diffuses away, leaving dangling bonds that act as electron-accepting trap site at an energy level mid-way between the valence and conduction bands. These sites dramatically increase the probability of an electron to be excited into the conduction band, i.e. increase the thermally generated dark current from the surface. Therefore, X-ray radiation reverses the annealing process done in manufacture.

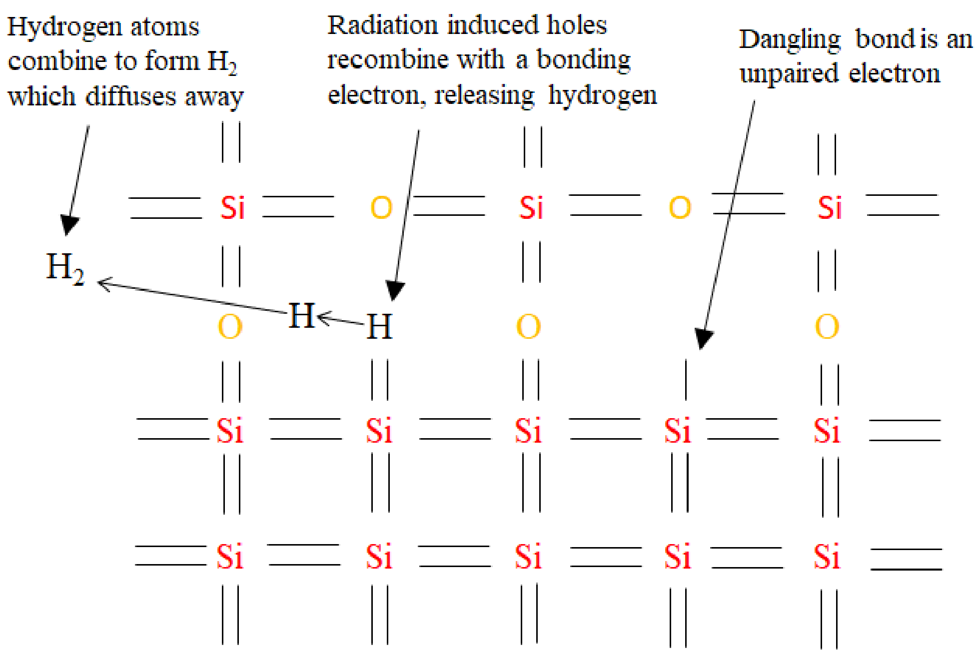

Figure 5. The atomic structure at the Si-SiO_2 interface of a CCD showing the release of molecular hydrogen due to radiation induced surface traps and the resulting dangling bonds.

It follows that the surface dark current will increase as the dose of X-rays increases due to radiation induced surface traps described above. By irradiating an EM-CCD with a known dose of X-rays the response can be monitored. Any increase in dark current can therefore be put into context with regards to an expected lifetime on a RIXS beamline.

5. Experimental setup and results

In order to test the response of EM-CCDs to X-ray radiation, two CCD97s [20] were taken to PTB at the BESSY II synchrotron in Berlin. The aim of this investigation was to irradiate the CCDs with a range of doses and X-ray energies that encourage damage at the back-surface and front surfaces of the device. The dark current increase in each irradiated region can then be monitored. The typical operational temperature of EM-CCDs on a RIXS beamline is < -90 °C, but here the CCD97s were operated at -44 °C which allowed the dark current to be accurately measured using practically short integration times.

The EM-CCDs were used in Non Inverted Mode Operation (NIMO) so that the dark current was not suppressed. The initial photon energy of the X-ray was chosen to be 90 eV. At this energy, 3% of X-rays can penetrate further than 2 μm in the silicon lattice. Therefore, most will be absorbed close to the surface of the CCD. As the CCD97 is back illuminated, the X-rays of this energy will be absorbed away from the front surface $Si\text{-}SiO_2$ interface where damage is most likely to occur. A fluence of $8.28\text{x}10^8$ photons/mm^2 (2.56 Gy) at 90 eV resulted in no detectable increase in dark current.

In order to increase the penetration of the X-rays and probe damage at the front surface, near to the $Si\text{-}SiO_2$ interface, the energy of X-rays was increased to 1800 eV. The thickness of silicon in the image region of the CCD was taken to be 13 ± 1 μm. Figure 6 shows the transmission of X-ray photons of various energies through 12 and 14 μm silicon [21]. For 1800 eV, the transmission through 12 μm is 41% and the transmission through 14 μm is 36%. Therefore, approximately 5% of incident X-rays will be absorbed within 1 μm of the $Si\text{-}SiO_2$ interface.

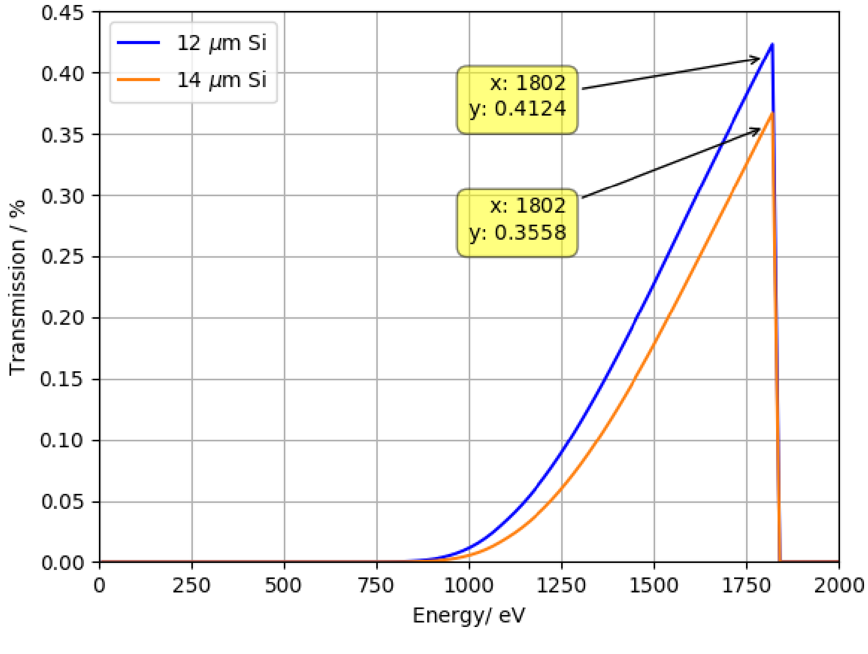

Figure 6. Transmission through 12 μm and 14 μm silicon at a range of X-ray energies. The transmission for ~1800 eV photons for both thicknesses are shown.

The EM-CCDs were irradiated and then monitored for a period of time after the irradiation had finished. This was done so that any change in dark current could be measured. When monitoring the images after irradiation, the signal level in the region that had been irradiated appeared to be reducing. Figure 7(a) shows an example image that was taken 13 s after irradiating with a fluence of 1.38×10^{12} photons/mm^2. Figure 7(b) shows the same CCD but taken 60 s after irradiation. The bright rectangle represents the irradiated region, and shows that the dark current level decreases with time after the irradiation finishes. In total, four different doses of 1800 eV X-rays were given to two devices. For each of these irradiations, the dark current was monitored after the irradiation had finished.

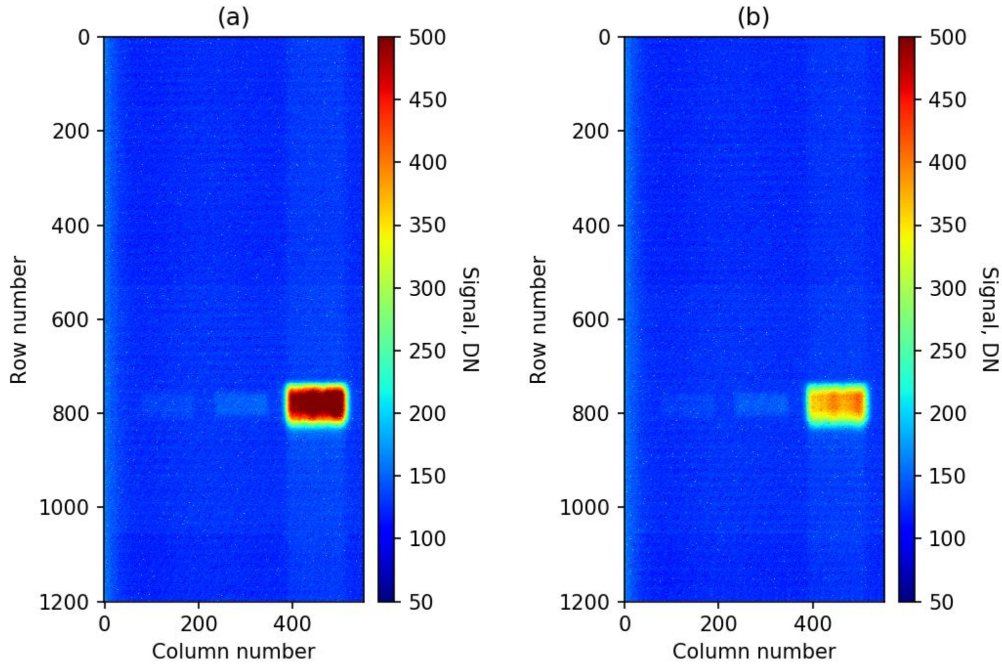

Figure 7. (a) A raw image taken from a CCD97 13 seconds after a fluence of 1.38×10^{12} photons/mm^2. (b) An image of the same CCD97 60 seconds after the irradiation. Dark signal generated in the irradiated region (bright rectangle centred at column 450 and row 800) visibly decreases during the 47 seconds between these images. The increase in dark current from other irradiations are visible in both images by a less pronounced, but still visible, rectangle. One is centred at column 150 and row 800, and the other is centred at column 300 and row 800

Figure 8 shows that the dark current decreases with time for all doses. In addition, the shape of the curve is independent of dose. On further investigation, the decrease in dark current is shown to be comprised of two exponential components with different decay time constants. One has a short half-life which is approximately 20 s. The second exponential has a longer half-life of 275 ± 75 s. The two exponential components suggest that there are different dark current generation mechanisms. One proposed source is two different types of interface traps, such as P_{b0} and P_{b1} [9], acting as dark current generation centres that may anneal at different rates. Another source of signal is the release of trapped charge from deep within the oxide, which could contribute to a release of charge with an exponential decay. Further work is required varying the operating temperature to explore the different dark current exponentials.

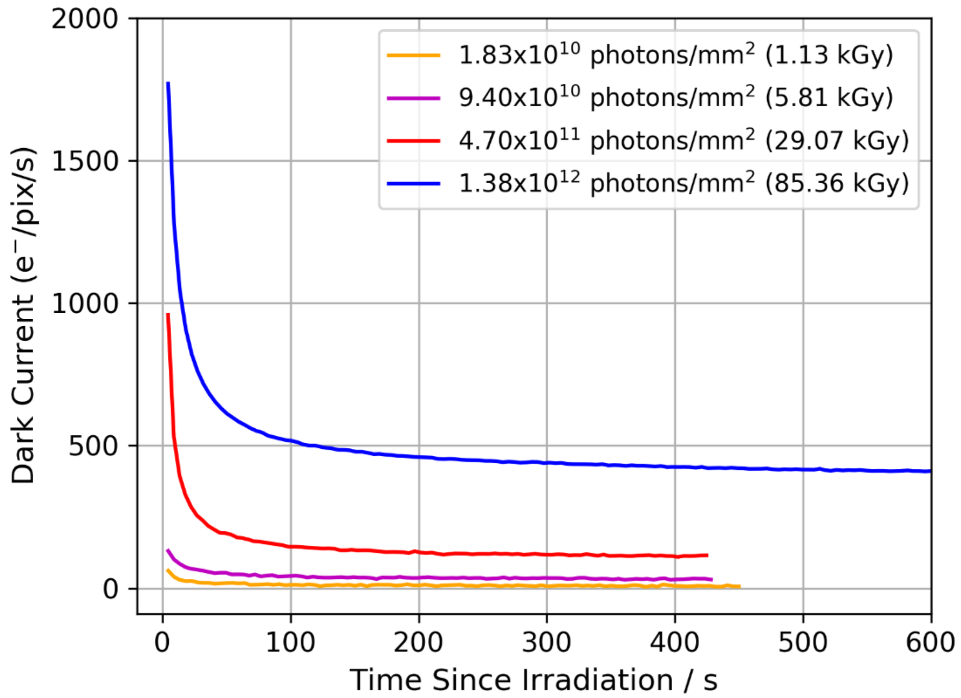

Figure 8. The dark current in each irradiated region shown against the time since the irradiation had finished. The legend shows the photon flux density for each of the irradiations as well as the corresponding dose. The dose was calculated by finding the energy deposited in a volume of 1 mm x 1 mm x 2 µm of the EM-CCD and scaling up.

In order to be able to predict a lifetime for EM-CCDs when used on a RIXS beamline, the dose received on the testing of the CCD97s must be compared to that which they might receive during a RIXS experiment. The requirement of single photon events due to the need for centroiding to achieve the best resolution performance means that the flux incident onto the EM-CCD will be small. In order to estimate the lifetime of the EM-CCD, an assumption for the flux incident onto the detector has been made to be 1000 photon/mm^2/s (or 0.25 photon/pix/s). This flux rate can be considered an overestimate for the majority of RIXS experiments but it serves to put a lower limit on the lifetime of the device. Using 1800 eV photons, only 5% of the X-rays will interact at the Si-SiO$_2$ interface if the X-rays are incident normal to the device surface. In addition, the EM-CCDs have been assumed to be used continuously for 75% of the year. With these two assumptions, the time taken for the EM-CCD to have received 1.83x10^{10} photons/mm^2 at the Si-SiO$_2$ interface is approximately 16 years. This corresponds to the lowest of the doses given to an EM-CCD in the radiation damage experiment which saw an initial increase in the dark current up to 60 e$^-$/pix/s which reduced to 6 e$^-$/pix/s after 8 minutes (at -44 ˚C).

RIXS experiments are usually operated at a much shallower X-ray incidence angle than the 90° that was used throughout the analysis above. A typical angle used is 20°, which means that the X-rays have to pass through more silicon in order to reach the Si-SiO$_2$ interface. At this angle, approximately 1% of X-rays will interact close to the Si-SiO$_2$ interface. Therefore, it would take 79 years to see an increase in the dark current up to 6 e$^-$/pix/s (at -44 ˚C). The numbers here are calculated using 1800 eV X-rays which can penetrate silicon easily compared to X-rays of lower energy as shown in Figure 6. When using X-rays of a lower energy, the time taken to see any increase in dark current will also increase.

During this experiment, the CCDs were operated in NIMO mode so that the dark current is not supressed. In normal use, the CCDs are operated with a substrate voltage of 6 V which is closer to inversion. As a result, the dark current will be supressed and will have less of an effect. Therefore, during normal operation on a RIXS beamline, radiation damage will have no effect on the performance of the EM-CCDs.

6. Conclusions

Past work on the resolution improvements using EM-CCDs has shown that they are well suited to work on a RIXS beamline. This has led to their adoption in the newest generation of RIXS cameras. However, the effect of soft X-ray radiation damage on EM-CCDs is not well understood, although the prime candidate for any damage is understood to be the creation of surface traps at the Si-SiO_2 interface.

Irradiating the back surface of an EM-CCD with a fluence of 8.28×10^8 photons/mm^2 (2.56 Gy) at 90 eV did not show any increase in the dark current in the irradiated region. The result of irradiating two EM-CCDs with varying doses of soft X-rays with an energy of 1800 eV has shown to increase the dark current in the irradiated region. Taking the minimum fluence of 1.83×10^{10} photons/mm^2 (1.13 kGy) the initial dark current rose to a maximum of 60 e^-/pix/s and immediately began to decrease to 6 e^-/pix/s after 8 minutes. A similar reduction of dark current was seen in the other three doses and the shape of the dark current decay is described by two exponential components in each case. The source of the dark current decay is currently unknown, however two explanations have been proposed. One explanation is the release of trapped charge following irradiation, and the other is the annealing of dark current generation centres which may have different annealing time constants.

The results discussed in this paper show that X-ray radiation can cause damage to EM-CCDs. For a worst-case estimate of a RIXS experiment using penetrating 1800 eV X-rays at a 90° incidence angle, it would take 16 years for an increase of dark current to 6 e^-/pix/s. At a more typical incident angle of 20° this becomes 79 years in order to see the same increase in dark current. Therefore, with low incident angles, an EM-CCD used in a RIXS experiment would have to be operated for decades before any increase in dark current was seen, meaning there is no concern for radiation damage.

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